



(19) Eur pâisches Patentamt
Eur p an Patent Office
Office eur péen des brevets



(11) Publication number:

0 503 507 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 92103901.2

(51) Int. Cl.⁵: A61K 7/06, A61K 7/13

(22) Date of filing: 06.03.92

(30) Priority: 08.03.91 JP 43782/91

(71) Applicant: Kao Corporation
1-14-10, Nihonbashi Kayaba-cho
Chuo-ku Tokyo(JP)

(43) Date of publication of application:
16.09.92 Bulletin 92/38

(72) Inventor: Yoshihara, Toru
8-1-8-101, Kameido, Koto-ku
Tokyo(JP)
Inventor: Misu, Daisuke
Gartenstrasse 42
W-6102 Pfungstadt-Hahn(DE)

(84) Designated Contracting States:
AT CH DE LI NL

(74) Representative: Wächtershäuser, Günter, Dr.
Tal 29
W-8000 München 2(DE)

(54) **Dye composition for keratinous fibers.**

(57) A dye composition for keratinous fibers comprising (a) a direct dye, (b) one or more polymers selected from the group consisting of cationic polymers and amphoteric polymers, (c) a betaine derivative, and (d) an organic solvent. The dye compositions exhibits a superior dyeing ability and an excellent conditioning effect which is maintained for a long period of time with repeated shampooing.

EP 0 503 507 A1

BACKGROUND OF THE INVENTIONField of the Invention:

5 The present invention relates to a dye composition for keratinous fibers, and, in particular, to a dye composition providing a long-lasting excellent conditioning effect.

Description of the Background Arts:

10 Most popular oxidative hair dyes consist essentially of an oxidative dyestuff and an oxidizing agent. Since they are used together with hydrogen peroxide under alkaline conditions, the dyeing operation involves risks of damaging hair and of giving primary irritation to the skin, producing red spots, small blisters, and the like. In order to eliminates these risks to scalps and hairs by oxidative dyeing, semipermanent hair dyes comprising a direct dye and imparting less adverse effects to scalps and hairs
15 have been developed.

Problems in these semipermanent hair dyeing compositions are providing unfavorable feelings upon finish because of a comparatively large amount of solvents contained therein. Hairs treated with these dye compositions cannot be combed smoothly with finger; they are rather hard and less slippery.

20 Japanese Patent Laid-open (ko-kai) No. 50145/1974 discloses a semipermanent hair dye composition in which a quarternary amine compound and an N-oxyalkylated long chain fatty acid amide are used in combination, claiming that the composition improves the feel of hair and prevents hair from being entangled, thus ensuring its easy combing. A problem in this type of hair dye composition was that it tends to be removed so easily from the hair by shampooing that its effects do not last long.

25 British Patent No. 2173515 discloses a method of promoting a hair conditioning effect by the combined use of a direct dye, a cationized silicone active agent, and a hydroxylated silicone derivative. The composition, however, has a problem that the conditioning effect does not last over a sufficient period time because a hydroxylated silicone derivative is easily removed from the hair.

30 Japanese Patent Laid-open (ko-kai) No. 157713/1983 discloses a hair dye composition comprising 0.5-10% of water-soluble cationic polymer and 0.5-30% of water-soluble anionic surfactant. The Patent Application claims that the hair dye composition can withstand several times of shampooing and provides an excellent hair-set effect. However, the combination of the polymers and the surfactants cannot provide a sufficiently long-lasting conditioning effect.

35 There have been no dye composition for keratinous fibers using a direct dye which provides a good feel and a long-lasting excellent conditioning effect which is not lost by shampooing or the like. Development of such a composition has earnestly been desired.

In view of this situation the present inventors have undertaken extensive studies and found that a composition exhibiting a long-lasting excellent hair conditioning effect can be obtained by incorporating a betaine derivative in a direct dye composition together with a cationic polymer or an amphoteric polymer. This finding has led to the completion of the present invention.

SUMMARY OF THE INVENTION

40 Accordingly, an object of the present invention is to provide a dye composition for keratinous fibers comprising (a) a direct dye, (b) one or more polymers selected from the group consisting of cationic polymers and amphoteric polymers, (c) a betaine derivative, and (d) an organic solvent.

45 Other objects, features and advantages of the invention will hereinafter become more readily apparent from the following description.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

50 Direct dyes which can be used in the present invention are any dyes which can directly dye keratinous fibers in a dying bath without using mordants. They may be nitro dyes, basic dyes, or disperse dyes. Specific examples of nitro dyes are 3-amino-4-hydroxynitrobenzene, 2-amino-5-hydroxynitrobenzene, 2-amino-3-hydroxynitrobenzene, 2-amino-5-N,N-bis- β -hydroxyethylaminonitrobenzene, 2-amino-4-chloro-5-N- β -hydroxyethylaminonitrobenzene, 2-amino-4-methyl-5-N- β -hydroxyethylaminonitrobenzene, 3,4-bis-(N- β -hydroxyethylamino)nitrobenzene, 2-amino-4-methyl-5-N- β , γ -dihydroxypropylaminonitrobenzene, 2-amino-4-methyl-5- β -aminoethylaminonitrobenzene, 2-amino-4-hydroxynitrobenzene, and the like. Furthermore, given as particularly preferable dyes are 3,4-diaminonitrobenzene, 2,5-diaminonitrobenzene, 2-amino-5- β -N-

hydroxyethylaminonitrobenzene, 2-N- β -hydroxyethylamino-5-N,N-bis- β -hydroxyethylaminonitrobenzene, 2-N-methylamino-5-N-methyl-N- β -hydroxyethylaminonitrobenzene, 2-N- β -hydroxy thylamino-5-hydroxynitrobenzen, 3-methoxy-4-N- β -hydroxyethylaminonitrobenzene, (nitro-4-methylamino-3)ph noxyethanol, 2-N- β -hydroxyethylamino-5-aminonitrobenzene, 2-N- β -hydroxyethylaminonitrobenzene, 3-amino-4-N- β -hydroxyethylaminonitrobenzene, 3- β -hydroxyethyloxy-4-N- β -hydroxyethylaminonitrobenzene, 2-amino-5-N-methylaminonitrobenzene, 2-amino-3-methylnitrobenzene, 2-N- β -hydroxyethylamino-5- β , γ -dihydroxypropoxyoxynitrobenzene, 3-hydroxy-4-aminonitrobenzene, 3-hydroxy-4-N- β -hydroxyethylaminonitrobenzene, 2,5-N,N'- β -hydroxyethylaminonitrobenzene, 2-N-methylamino-4-o- β , γ -dihydroxypropoxyoxynitrobenzene, 2-N- β -aminoethylamino-5-N,N-bis-(β -hydroxyethyl)aminonitrobenzene, 2-N- β -aminoethylamino-4-methoxynitrobenzene, 2-N- β -aminoethylamino-5- β -hydroxyethyloxynitrobenzene, 1-amino-4-methylaminoanthraquinone, 1,4-diaminoanthraquinone, and the like.

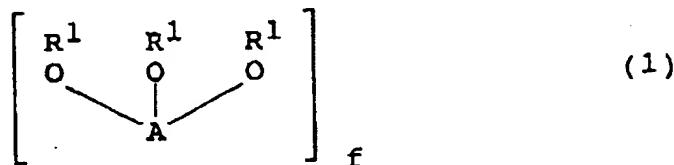
Examples of basic dyes are Siena Brown, Mahogany, Madder Red, Steel Blue, Straw Yellow (all trademarks, products of William Co.), and the like. Given as examples of disperse dyes are Disperse Black 9, Disperse Blue 1, Disperse Violet 1, Disperse Violet 4 (all described in Cosmetic Ingredient Dictionary, U.S.A.), and the like. These dyes are incorporated in the composition of the present invention in an amount of 0.05-3% by weight ("% by weight" is hereinafter simply referred to as "%"), preferably 0.1-1%, although a specific amount is determined within this range depending upon the color of the dye.

Cationic polymers which is component (b) in the composition of the present invention may be cationized cellulose derivatives, cationic starch, cationized guar-gum derivatives, copolymers of diallyl quaternary ammonium salt and acrylamide, polymers of diallyl quaternary ammonium salt, quaternarized polyvinylpyrrolidone derivatives, cationic silicone polymers, and the like.

As a cationic cellulose derivative, a compound represented by the following formula (1) is desirable.

25

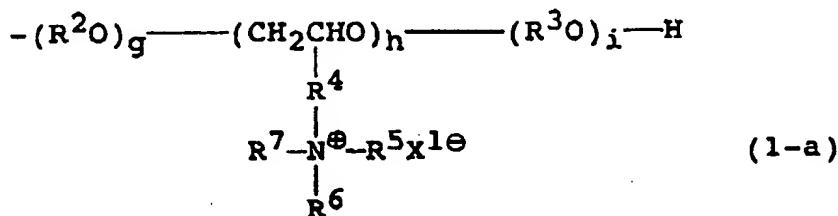
30



wherein A indicates a residual group of anhydroglucose unit, f is an integer of from 50 to 20,000, and each R¹ independently represents a substitution group of the following formula (1-a).

40

45



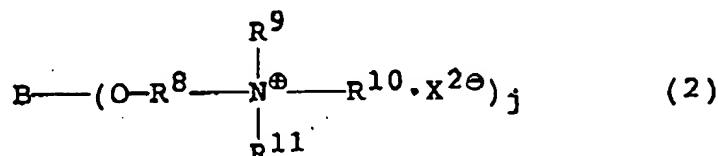
wherein R² and R³ are individually an alkylene group with 2-3 carbon atoms, g is an integer of 0-10, h is an integer of 0-3, i is an integer of 0-10, R⁴ represents an alkylene group or a hydroxyalkylene group with 1-3 carbon atoms, R⁵, R⁶, and R⁷ may be the same or different and represent an alkyl, aryl, or aralkyl group with not more than 20 carbon atoms and may form a heterocyclic ring together with a nitrogen atom in the formula, and X¹ denotes an anion; e.g., chlorine, bromine, iodine, sulfate, sulfonate, methylsulfate, phosphate, nitrate, or the like.

The degree f cation substitution of the cationic cellulose, that is, the average value of h for each anhydroglucose unit is preferably between 0.01 to 1, with the range of 0.02 to 0.5 being more preferable. The sum of (g + i) averages between 1 and 3. A substitution value of less than 0.01 is unsatisfactory; while a value greater than 1 is with no particular problem, even though a value smaller than 1 is more desirable from the aspect of reaction yield. With respect to R⁵, R⁶, and R⁷, compounds with methyl groups for all of them or compounds with a C₁₀₋₁₈ long chain alkyl group for one of them and C₁₋₃ short chain alkyl group

for others are preferable. A preferable molecular weight of the cationic cellulose used here is in the range of about 100,000 to 8,000,000.

A desirable cationic starch for use in the present invention has the following formula (2).

5



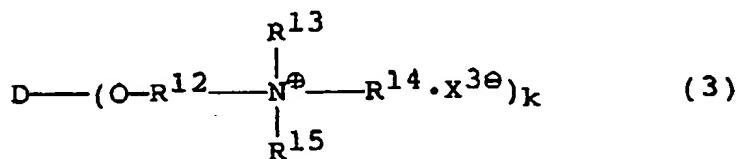
10

wherein B represents a starch residual group, R⁸ represents an alkylene group or a hydroxyalkylene group, R⁹, R¹⁰, and R¹¹ may be the same or different and represent an alkyl, aryl, or aralkyl group with not more than 10 carbon atoms and may form a heterocyclic ring together with the nitrogen atom in the formula, X² represents an anion; e.g., chlorine, bromine, iodine, sulfate, sulfonate, methylsulfate, phosphate, nitrate, or the like, and j is a positive integer.

The degree of cation substitution of the cationic starch, i.e., the number of cation groups for each anhydrous glucose group is desirably 0.01 to 1, with more desirable range being 0.02 to 0.5. A substitution value of less than 0.01 is unsatisfactory; while a value greater than 1 is with no particular problem, even though a value smaller than 1 is more desirable from the aspect of reaction yield.

Preferable cationized guar-gum derivatives are compounds of the following formula (3).

25



30

wherein D represents a guar-gum residual group, R¹² represents an alkylene group or a hydroxyalkylene group, R¹³, R¹⁴, and R¹⁵ may be the same or different and represent an alkyl, aryl, or aralkyl group with not more than 10 carbon atoms and may form a heterocyclic ring together with the nitrogen atom in the formula, X³ represents an anion; e.g., chlorine, bromine, iodine, sulfate, sulfonate, methylsulfate, phosphate, nitrate, or the like, and k is a positive integer.

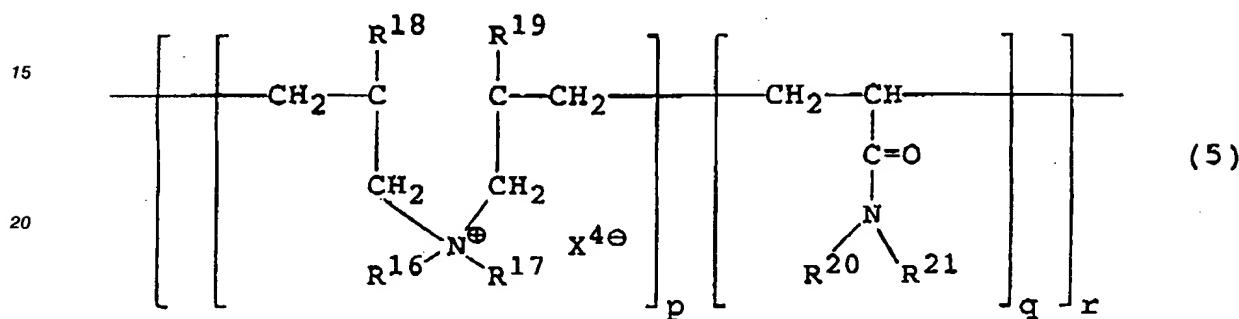
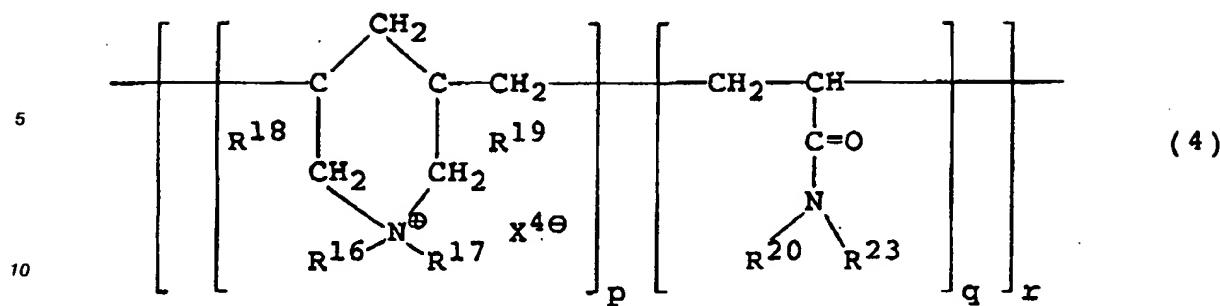
The degree of cation substitution of the cationic guar-gum, i.e., the number of cation groups for each glucose group, is desirably 0.01 to 1, with more desirable range being 0.02 to 0.5. This type of cationized polymers are described, for example, in Japanese Patent Publication (ko-koku) Nos. 35640/1983 and 46158/1985, and Japanese Patent Laid-open (ko-kai) No. 53996/1983, and commercially available under the trademark of Jaguarh (products of Cellenese Stein-Hohl Co.).

Desirable polymers of cationized diallyl quaternary ammonium salt and copolymers of cationized diallyl quaternary ammonium salt and acryl amide for use in the present invention are those represented by the following formulae (4) and (5).

45

50

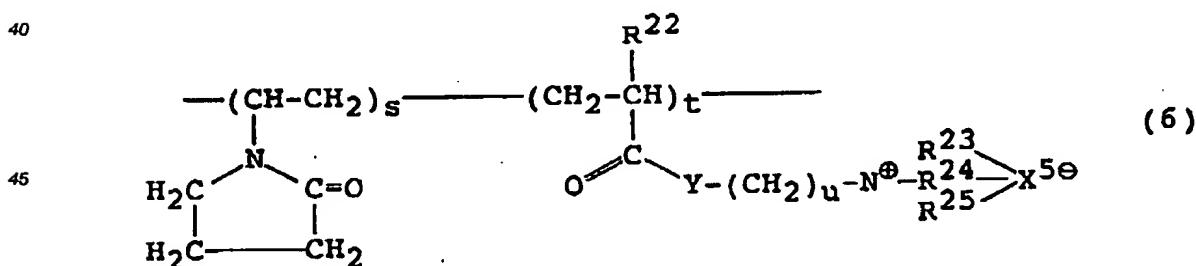
55



25 wherein R¹⁶ and R¹⁷ may be the same or different and each independently represents a hydrogen, an alkyl group with 1-18 carbon atoms, a phenyl group, an aryl group, a hydroxyalkyl group, an amidoalkyl group, a cyanoalkyl group, an alkoxyalkyl group, or a carboalkoxyalkyl group, R¹⁸, R¹⁹, R²⁰, and R²¹ may be the same or different and each independently represents a hydrogen, a lower alkyl group with 1-3 carbon atoms, or a phenyl group, X⁴ represents an anion; e.g., chlorine, bromine, iodine, sulfate, sulfonate, methylsulfate, phosphate, nitrate, or the like, p is an integer of 1-50, q is an integer of 0-50, and r is an integer of 150-8,000.

30 The molecular weights of the polymers of diallyl quaternary ammonium salt and the copolymers of diallyl quaternary ammonium salt and acryl amide may be in the range of 30,000-2,000,000, with the range 35 100,000-1,000,000 being preferable.

35 Preferable quaternary polyvinylpyrrolidone derivatives used in the present invention are compounds of the following formula (6).

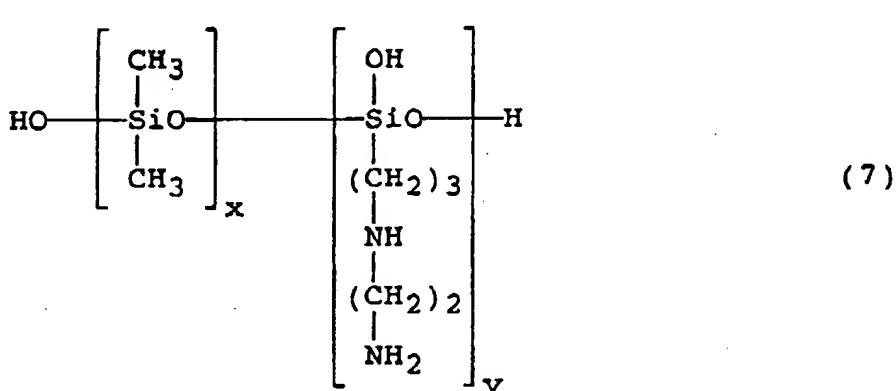


50 wherein R²² represents a hydrogen atom or an alkyl group with 1-3 carbon atoms, R²³, R²⁴, and R²⁵ may be the same or different and each independently represents a hydrogen, a C₁₋₄ alkyl, hydroxyalkyl, amidoalkyl, cyanoalkyl, alkoxyalkyl, or carboalkoxyalkyl group, Y represents an oxygen atom or an NH group in the amide bond, X⁵ represents an anion; e.g., chlorin, bromine, iodin, sulfate, sulfonate, an alkylsulfat with 1-4 carbon atoms, phosphate, nitrate, or the like, u is an integer of 1-10, and s and t are integers satisfying the equation s + t = 20 to 8,000.

55 A preferable molecular weight of the quaternary polyvinylpyrrolidone derivatives is in the range of about 10,000-2,000,000, with a particularly preferable range being 50,000-1,500,000.

A preferable amount of cationic nitrogen of the cationic polymer contained in the above vinyl polymers is 0.004-0.2%, and preferably 0.01-0.15%, of the vinyl polymer. If the amount of the cationic nitrogen is smaller than 0.004%, the effects of the present invention is not sufficiently exhibited. The amount exceeding 0.2% may cause the vinyl polymer color and is unconomical, even though a good performance can be provided by such an excess amount.

Given as typical cationic silicone polymers are polymers having an average molecular weight of 3,000-100,000 and represented by the following formula (7).



25 wherein x and y are integers depending on the molecular weight.

Cationic silicone polymers of the above formula (7) are described in the name of Amodimethicone in CTFA Dictionary, third edition (Cosmetic Ingredient Dictionary, USA). It is desirable that these cationic silicone polymers be used in a form of an aqueous emulsion. Such an emulsion can be obtained, for example, according to the method described in Japanese Patent Publication (ko-koku) No. 38609/1981, by the emulsion polymerization of a cyclic diorganopolysiloxane and an organodialkoxysilane having an aminoalkyl group and a hydroxy, hydroxy alkyl, oxyalkylene, or polyoxyalkylene group, in the presence of a quaternary ammonium salt surfactant and water.

Amphoteric polymers, another component (b) of the hair dye composition of the present invention, can be obtained by the copolymerization of acidic vinyl monomer and basic vinyl monomer, or by the polymerization of amphoteric monomer, or by introducing an acidic group, a basic group, or both, or an amphoteric group into a synthetic or natural polymer depending on its characteristics.

Examples of such amphoteric polymers are as follows.

(1) Copolymers of acidic vinyl monomer and basic vinyl monomer

46 Typical examples are amphoteric polymers prepared by the copolymerization of a mixture of 45-55 mol% of acidic vinyl monomer or its salt and 45-55 mol% of basic vinyl monomer at 150°C in the presence of a known radical polymerization initiator or a known accelerator. The mol% here applies to the case where each vinyl monomer possesses one acidic or basic group. In the case where monomers have two or more acidic or basic groups, the mole % must be adjusted so as to make the net electronic charge zero.
45

An acidic vinyl monomer is defined as a compound having an acidic group, e.g., carboxylic, sulfonic, or phosphoric group, and a polymerizable vinyl group in a molecule. Examples of such compounds are monobasic unsaturated acids, such as acrylic acid, methacrylic acid, crotonic acid, vinyl benzoic acid, 2-acrylamide-2-methylpropanesulfonic acid, styrenesulfonic acid, vinylsulfonic acid, allylsulfonic acid, methacrylsulfonic acid, and 3-methacrylpropanesulfonic acid; dibasic unsaturated acids, such as itaconic acid, maleic acid, and fumaric acid; and monoesters of these mono- or dibasic unsaturated acids.

Basic vinyl monomers are compounds having a basic group, e.g., primary, secondary, or tertiary amino group, and a polymerizable vinyl group in a molecule, such as dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, dimethylaminoethyl acrylate, diethylaminoethyl acrylate, dimethylaminopropyl acrylate, dimethylaminopropyl methacryl amide, 2-vinylpyridine, 4-vinylpyridine, dimethylallylamine, and diallylmethylamine, as well as quarternarized compounds thereof.

Quaternary compounds here are used to denote hydrides, or methylated or ethylated compounds having a counter anion such as halogen ion, e.g., chlorine or bromine ion; hydroxide ion, methylsulfonat

group, or the like.

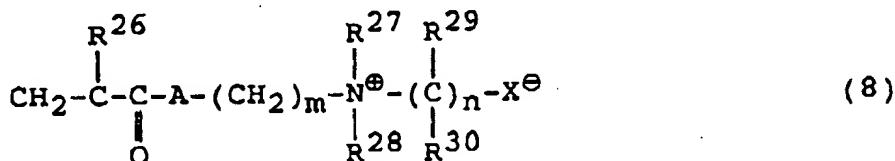
It is possible to incorporate any copolymerizable vinyl monomers other than the acidic or basic vinyl monomers as a third component in the copolymerization. The proportion of such other vinyl monomers must be less than 60 mol%.

5 Vinyl monomers other than the acidic or basic vinyl monomers are monomers polymerizable by a radical polymerization initiator and include such compounds as acrylates, e.g., methyl acrylate, ethyl acrylate; styrene compounds, e.g., styrene, α -methylstyrene; acrylic amide, methacrylic amide, vinyl ether, vinyl acetate, and the like.

10 (2) Polymers of amphoteric compounds

Typical examples are amphoteric polymers prepared by polymerizing amphoteric monomers represented by the following formula (8) at 20-130°C in the presence of a radical polymerization initiator.

15



20

wherein R^{26} , R^{29} , and R^{30} individually represent a hydrogen atom or a methyl group, R^{27} and R^{28} individually represent a methyl or ethyl group, A is $-\text{O}-$ or $-\text{NH}-$, X is $-\text{CO}_2-$, $-\text{SO}_3-$ or $-\text{PHO}_3-$, and m and n are integers of 1-3.

25 Amphoteric monomers of formula (8) can be synthesized by a reaction of an aminoalkyl ester or an aminoalkyl amide of acrylic acid or methacrylic acid and lactone, sultone, or cyclic phosphite.

Specific examples of such monomers include 3-dimethyl(methacryloyloxyethyl)ammoniumpropane sulfonate, 3-dimethyl(methacryloylamidepropyl)ammoniumpropane sulfonate, and the like.

30

It is possible to incorporate any copolymerizable vinyl monomers other than these amphoteric monomers as a third component. The proportion of such other vinyl monomers must be less than 60 mol%. Such other vinyl monomers are monomers polymerizable by a radical polymerization initiator and include such compounds as acrylates, e.g., methyl acrylate, ethyl acrylate; methacrylates, e.g., methyl methacrylate, ethyl methacrylate; styrene compounds, e.g., styrene, α -methylstyrene; acrylic amide, methacrylic amide, vinyl ether, vinyl acetate, and the like.

35

The above cationic or amphoteric polymers may be used alone or two or more of them may be used in combination as component (b). Particularly preferable cationic or amphoteric polymers are homopolymers of diallyl quaternary ammonium salt, i.e., homopolymers of formulas (5) or (6), wherein $q=0$. An amount of components (b) to be formulated in the composition of the present invention is preferably 0.01-10%, and particularly preferably 0.1-5%. If the amount of component (b) is smaller than this range, the composition cannot provide a long-lasting conditioning effect. An amount exceeding this range will not give an effect proportionate to the excess amount.

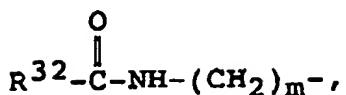
40 As examples of betaine-type surfactants; component (c) of the composition of the present invention, compounds of the following formulas (9) and (10) are given.

45

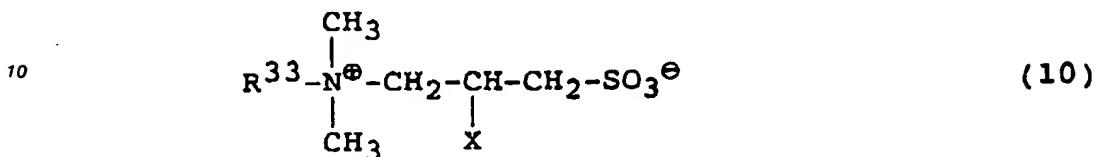


50

wherein R^{31} is a linear or branched alkyl group having 10-24 carbon atoms, or a group represented by formula,



5 wherein R³² is a linear or branched alkyl group having 9-23 carbon atoms and m is an integer of 1-5.



15 wherein R³³ is a linear or branched alkyl group having 10-24 carbon atoms, or a group represented by formula,



wherein R³⁴ is a linear or branched alkyl group having 9-23 carbon atoms and n is an integer of 1-5; and X
25 is a hydrogen or a hydroxy group.

Specific examples of the betaine-type surfactants are cocamidopropylbetaine, oleamidopropylbetaine, lauramidopropylbetaine, cocobetaine, oleylbetaine, laurylbetaine, cetylbetaine, cocamidopropylhydroxy sulfain, lauryl saltain, and the like. Of these especially preferable are cocamidopropylbetaine, lauramidopropylbetaine, and the like. Here, "coco" means fatty acid mixtures of which the major components are C₁₂ fatty acids derived from coconut oil.

The amount of components (c) to be formulated in the composition of the present invention is preferably 0.1-0.5%. An amount outside this range does not give the intended long-lasting conditioning effect.

There are no limitations as to organic solvents (d) used in the composition of the present invention, so long as the solvent can dissolve components (b), cationic polymer, etc., and betaine derivatives (c). Examples of preferable organic solvents include ethanol, iso-propanol, n-propanol, n-butanol, iso-butanol, ethylene glycol, propylene glycol, 1,3-butanediol, benzyl alcohol, cinnamyl alcohol, phenetyl alcohol, p-anisyl alcohol, p-methylbenzyl alcohol, phenoxy ethanol, 2-benzoyloxy ethanol, methyl carbitol, ethyl carbitol, propyl carbitol, butyl carbitol, triethylene glycol monoethyl ether, triethylene glycol monobutyl ether, 40 glycerin, N-methylpyrrolidone, N-octylpyrrolidone, N-laurylpyrrolidone, and the like. They may be used alone or two or more of them may be used together.

Complexes of components (b) and (c) dissolved in the organic solvent, are diluted when hair is rinsed, and deposit on the hair, thus exhibiting excellent conditioning effects. In order to promote the deposition of complexes on the hair, the solvent is desirably used as a mixture with water. A preferable proportion of the solvent and water is in the range of 20:80-50:50, although a specific proportion depends on the solubility of the water-soluble complex in the solvent. If the proportion of water is too high, the complex tends to deposit in the aqueous system, thus impairing the conditioning effect. If the amount of water is too small or if no water is added at all, the amount of the complex deposited on the hair is insufficient, resulting in a reduced conditioning effect.

50 Other components which are commonly used in cosmetic compositions, such as thickeners (e.g., hydroxyethylcellulose), oil components (e.g., silicones), perfumes, preservatives, UV absorbers, antiseptics, and the like, may optionally be incorporated to the extent that they do not impair the effects intended in the present invention.

Other features of the invention will become apparent in the course of the following description of the exemplary embodiments which are given for illustration of the invention and which are not intended to be limiting thereof.

EXAMPLES

In the examples below in order to evaluate compositions of the present invention and comparative compositions 2.5 g of each composition was applied to a tress of blond hair weighing about 5 g, left for 30 minutes at 30°C, washed with a stream of water, shampooed and rinsed, and dried. The tresses were evaluated 5 expert pan lists on the following items.

5

(1) Smoothness

- AAA: Much smoother than untreated hair.
- BBB: Smoother than untreated hair.
- 10 CCC: The smoothness is equivalent to untreated hair.
- DDD: Less smooth than untreated hair.

(2) Feel of combing

- 15 AAA: Can be combed much better than untreated hair.
- BBB: Can be combed better than untreated hair.
- CCC: Can be combed as well as untreated hair.
- DDD: Combed worse than untreated hair.

20 (3) Feel of finger combing

- AAA: Can be combed with finger much better than untreated hair.
- BBB: Can be combed with finger better than untreated hair.
- CCC: Can be combed with finger as well as untreated hair.
- 25 DDD: Combed with finger worse than untreated hair.

(4) Feel of touch

- 30 AAA: The feel is much better than untreated hair.
- BBB: The feel is better than untreated hair.
- CCC: The feel is equivalent to untreated hair.
- DDD: The feel is worse than untreated hair.

Each of the dyed hair tresses was divided into two portions; one of the portions was shampooed, rinsed, and dried 5 times for comparison with another portion which has not been shampooed on the following 35 items.

(1) Smoothness

- 40 AAA: The smoothness is equivalent to non-shampooed hair.
- BBB: Slightly less smooth than non-shampooed hair.
- CCC: Less smooth than non-shampooed hair.
- DDD: Considerably less smooth than non-shampooed hair.

(2) Feel of combing

- 45 AAA: Can be combed as well as non-shampooed hair.
- BBB: Combed slightly worse than non-shampooed hair.
- CCC: Combed worse than non-shampooed hair.
- DDD: Combed considerably worse than non-shampooed hair.

50 (3) Feel of finger combing

- AAA: Can be combed with finger as well as non-shampooed hair.
- BBB: Combed with finger slightly worse than non-shampooed hair.
- 55 CCC: Combed with finger worse than non-shampooed hair.
- DDD: Combed with finger considerably worse than non-shampooed hair.

(4) Feel of touch

AAA: The feel is equivalent to non-shampooed hair.
BBB: slightly drier feel than non-shampooed hair.
CCC: Drier feel than non-shampooed hair.
DDD: Considerably drier feel than non-shampooed hair.

5

Example 1

A dye (Steel Blue, 2-amino-5- β -N-hydroxyethylamino nitrobenzene) and Merquat 100 (Merck Co.) were dissolved in water. To the solution was added hydroxyethylcellulose suspended in a small amount of water,
10 and the mixture was heated to about 60°C to increase its viscosity. After cooling to room temperature, ethanol, ethyl carbitol, and Softazoline LPB (a product of Kawaken Fine Chemical Co.) were added. The mixture was stirred to homogenize to obtain a gel-like dye composition for keratinous fibers (Invention Product No. 1).

Invention Product Nos. 2-4 and Comparative product Nos. 1-3 were prepared in the same manner as
15 Invention product No 1.

The composition and the results of evaluation were shown in Tables 1-1 and 1-2, respectively. The results in Table 1-2 show a superior dyeing ability and a long-lasting excellent conditioning effect of Invention Products over Comparative Products.

20

25

30

35

40

45

50

55

TABLE 1-1 (Composition)

	Comparative product			Invention Product		
	1	2	3	1	2	3
Ethanol	20.0%	20.0%	20.0%	20.0%	20.0%	20.0%
Ethyl carbitol	10.0	10.0	10.0	10.0	10.0	10.0
Hydroxyethylcellulose	1.6	1.6	1.6	1.6	1.6	1.6
Merquat 100 (act. 40%) *1	0.3	0.3	-	0.3	-	-
Polymer JR-400 *2	-	-	0.3	-	0.3	-
Yukafoamer-AM-75 (act. 30%) *3	-	-	-	-	0.3	-
Merquat 550 (act. 8%) *4	-	-	-	-	-	0.3
Miranol C2MSP (act. 71%) *5	-	0.3	0.3	-	-	-
Softazoline LPB (act. 31%) *6	-	-	-	0.3	0.3	0.3
Steel Blue *7	0.1	0.1	0.1	0.1	0.1	0.1
Nitrobenzene	0.3	0.3	0.3	0.3	0.3	0.3
Water				Balance		

*1 Homopolymer of dimethylidiallyl ammonium chloride manufactured by Merck Co.

*2 Cationized cellulose manufactured by Union Carbide Corp.

*3 Copolymer of N-methacryloyloxyethyl-N,N-dimethylammonium- α -N-methyl carboxybetaine and butyl acrylate (act. 30%) manufactured by Mitsubishi Petrochemical Co., Ltd.

*4 Copolymer of dimethylidiallyl ammonium chloride and acryl amide manufactured by Merck Co.

*5 Cocoanaphorboxypropionate manufactured by Miranol Co.

*6 N-lauramidepropylbetaine manufactured by Kawaken Fine Chemical Co., Ltd.

TABLE 1-2 (Evaluation Results)

	Comparative product				Invention Product			
	1	2	3	4	1	2	3	4
<u>Immediately after dyeing</u>								
Smoothness	CCC	BBB	BBB	AAA	AAA	AAA	AAA	AAA
Feel of combing	CCC	BBB	BBB	AAA	AAA	AAA	AAA	AAA
Feel of finger combing	CCC	BBB	BBB	AAA	AAA	AAA	AAA	AAA
Feel of touch	CCC	CCC	CCC	AAA	AAA	BBB	BBB	BBB
<u>After 5 time shampooing</u>								
Smoothness	DDD	CCC	CCC	AAA	AAA	AAA	AAA	AAA
Feel of combing	DDD	CCC	CCC	AAA	AAA	AAA	AAA	AAA
Feel of finger combing	DDD	CCC	CCC	AAA	AAA	AAA	AAA	AAA
Feel of touch	DDD	DDD	DDD	AAA	BBB	BBB	BBB	BBB

Example 2

A dye composition for keratinous fibers was prepared from the following components in the same manner as the method for preparation of Invention Product No. 1.

	Ethanol	20.0%
5	Benzyl alcohol	5.0
	Hydroxyethylcellulose	1.6
10	Mergquat 100 *1	0.3
	Miratain CDMB *2	0.3
	2-amino-5-β-N-hydroxyethyl amino nitrobenzene	0.4
15	1-amino-2-β-N-hydroxyethyl amino nitrobenzene	0.1
	Perfume	0.2
20	Water	Balance

*1 Homopolymer of dimethyldiallylammonium chloride (act. 40%) manufactured by Merck Co.

*2 Cocobetaine (act. 37%) manufactured by Miranol Co.

30 5 g of the above composition was applied to a tress of blond hair weighing about 10 g, left for 30 minutes at 30°C, washed with tap water, shampooed and rinsed, and dried. The hair was dyed into a bright chestnut brown color, very smooth, and could be combed very well with finger. These effects were well kept even after 5 time shampooing.

35 Example 3

A dye composition for keratinous fibers was prepared from the following components in the same manner as the method for preparation of Invention Product No. 1.

40

45

50

55

	Ethanol	20.0%
5	Benzyl alcohol	5.0
	Hydroxyethylcellulose	1.6
10	Merquat 100 *1	0.3
	Miratain CB *2	0.3
	2-amino-5-β-N-hydroxyethyl amino nitrobenzene	0.3
15	Perfume	0.2
	Water	Balance
20	*1 Homopolymer of dimethyldiallylammonium chloride (act. 40%) manufactured by Merck Co.	
25	*2 Cocoamidepropylbetaine (act. 35%) manufactured by Miranol Co.	

30 5 g of the above composition was applied to a tress of blond hair weighing about 10 g, left for 30 minutes at 30 °C, washed with tap water, shampooed and rinsed, and dried. The hair was dyed into a blue color, very smooth, and could be combed very well with finger. These effects were well kept even after 5 time shampooing.

35 Example 4
 40 A dye composition for keratinous fibers was prepared from the following components in the same manner as the method for preparation of Invention Product No. 1.

45

50

55

	Ethanol	10.0%
5	1,3-Butanediol	10.0
	Benzyl alcohol	5.0
10	Hydroxyethylcellulose	1.6
	Merquat 100 *1	0.3
	Softazoline LPB *2	0.3
15	Silicone derivative	0.2
	Perfume	0.2
	Madder Red	0.3
20	Water	Balance

*1 Homopolymer of dimethyldiallylammonium chloride (act.

25 40%) manufactured by Merck Co.

*2 N-lauremidopropylbetaine (act. 31%) manufactured by

Kawaken Fine Chemical Co., Ltd.

30

5 g of the above composition was applied to a tress of blond hair weighing about 10 g, left for 30 minutes at 30°C, washed with tap water, shampooed and rinsed, and dried. The hair was dyed into a red color, very smooth, and could be combed very well with finger. These effects were well kept even after 5 time shampooing.

35 As illustrated above, the present invention provides dye compositions for keratinous fibers exhibiting a superior dyeing ability and an excellent conditioning effect which is maintained for a long period of time with repeated shampooing.

Obviously, numerous modifications and variations of the present invention are possible in light of the
40 above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

Claims

- 45 1. A dye composition for keratinous fibers comprising (a) a direct dye, (b) one or more polymers selected from the group consisting of cationic polymers and amphoteric polymers, (c) a betaine derivative, and (d) an organic solvent.
2. The composition according to Claim 1, wherein said component (b) is a polymer or copolymers of diallyl quaternary ammonium salt.